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3. Full name, address and postcode of the or of each applicant (underline all surnames)

Imerys Minerals Limited
John Keay House
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Cornwall PL25 4DJ
UK

04858 293 001.
Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation UK

4. Title of the invention
AN OPACIFIED POLYMER COMPOSITION

5. Name of your agent (if you have one) Haseltine Lake & Co.

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

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London
WC2B 6UD

Patents ADP number (if you know it) 34001

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Description

26

Claim(s)

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Abstract

1

Drawing(s)

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AN OPACIFIED POLYMER COMPOSITION

Field of the Invention

This invention relates generally to the use of a
5 flash calcined kaolin clay as an opacifier for a
polymer composition, and more particularly to the use
of flash calcined kaolin clay as a filler to fully or
partially replace the titanium dioxide filler which is
typically used as an opacifier in polyolefin polymer
10 compositions, and products or articles formed
therefrom. The invention also relates to methods of
making such compositions, to products such as films
formed from the polymeric compositions and to methods
of making such products.

15

Background of the Invention

The ability of a pigmented or filled polymer
system to diffuse and reflect a portion of the incident
light is known as its scattering power. The scattering
20 power of a pigment or filler is directly linked to its
hiding and opacifying power. The scattering power of a
filler or pigment is related to two properties,
refractive index and particle size distribution. The
greater the difference between the refractive indexes
25 of polymer and pigment or filler the greater the
scattering power, and therefore the greater the
opacity. TiO_2 rutile, with the highest refractive
index of all common pigments (of the order of 2.55 for
anatase and 2.7-2.75 for rutile), is the most efficient
30 scatterer and is well known as an opacifying white
pigment for polyolefin polymers, and in particular
polyethylene products such as polyethylene film.
However, titanium dioxide is an expensive material and
so it would be desirable to be able to replace some or
35 all of the titanium dioxide in polyolefin applications.
In this respect, one known replacement, or partial

replacement, opacifier is particulate calcium carbonate.

US-A-5571851 describes the use of silane treated calcined clays as reinforcing fillers for plastics systems such as polyamides.

Flash calcined kaolin clay, which is made by a process in which a hydrous kaolin clay is exposed to an elevated temperature for a short period of time, for example a few seconds, is already known as a filler for elastomer compositions, see GB-A-2067535. Flash calcined clay has also been used for many years as an extender for titanium dioxide in paints.

Brief Description of the Invention

According to a first aspect of the present invention, there is provided a polymer composition comprising a polymer resin, an amount of a flash calcined kaolin clay filler and an amount of a titanium dioxide filler, wherein the weight ratio of the flash calcined clay to the titanium dioxide in the composition is in the range of up to 10:1 and wherein the polymer resin is one which hardens or cures to a plastic material which has a refractive index of at least about 1.45.

The polymer composition may be prepared as a masterbatch composition, which may then be "let down" to an appropriate filler content before formation of the final polymeric product, such as a film product, from the polymer composition.

According to a second aspect of the invention, there is provided a production process for preparing a polymer composition of the first aspect of the invention in which the flash calcined kaolin clay and the titanium dioxide are mixed with the polymer resin to form a homogenous composition.

According to a third aspect of the present invention there is provided a polymer article made from the polymer composition of the first aspect of the present invention. For example, the polymer article may be a polyolefin film. Thus, in one embodiment, the present invention relates to a polyolefin film, preferably a polyethylene film, formed from a polymer composition of the first aspect of the invention.

The use of flash calcined kaolin clay in plastics which have a refractive index of at least about 1.45 permits the amount of titanium dioxide, which is a relatively expensive raw material, to be reduced, while retaining satisfactory product characteristics, particularly the opacity and whiteness of the product. This is of particular use for products such as polyolefin, e.g. polyethylene, film.

Without wishing to be bound by theory, it is believed that the refractive index of particulate flash calcined clay (which has been measured to be of the order of about 1.39) enables it to be used as an opacifier (and particularly as a partial replacement for a proportion of a titanium dioxide opacifier) in respect of polymer systems which have a refractive index greater than about 1.45, without the particle size having to be unacceptably high.

The term "particle diameter" used herein refers to a particle size measurement as determined by laser light particle size analysis using a CILAS (Compagnie Industrielle des Lasers) 1064 instrument. In this technique, the size of particles in powders, suspensions and emulsions may be measured using the diffraction of a laser beam, based on application of the Fraunhofer theory. The term "mean particle size" or "d₅₀" used herein is the value, determined in this way, of the particle diameter at which there are 50% by volume of the particles which have a diameter less than

the d_{50} value. The preferred sample formulation for measurement of particle sizes using the CILAS 1064 instrument is a suspension in a liquid. The CILAS 1064 instrument normally provides particle size data to two decimal places, to be rounded up or down when determining whether the requirements of the present invention are fulfilled.

Brief Description of the Drawings

Figure 1 shows opacity of polyethylene films made in Example 1 as a function of the level of the flash calcined kaolin clay for film with 3.6% TiO_2 . The broken line represents the value at 0% flash calcined clay and 4% TiO_2 .

Figure 2 shows the transmittance of films made in Example 1 containing 3.6 % by weight TiO_2 as a function of the level of flash calcined clay. The broken line represents the value at 0 % flash calcined clay, 4 % by weight TiO_2 .

Figure 3 shows the tensile strength (Elongation at break and Stress at break) properties in MD of polyethylene films made in Example 1 containing 3.6 % TiO_2 by weight as a function of the level of flash calcined clay. The data point at 0% flash calcined clay contains 4 % TiO_2 .

Figure 4 shows the opacity of TiO_2 :FCC films made in Example 2 as a function of FCC/ TiO_2 ratio, for FCCs with specific gravities ranging from 1.99 to 2.19.

Figure 5 shows the transmittance of TiO_2 :FCC films made in Example 2 as a function of ratio of FCC to TiO_2 for FCCs with specific gravity ranging from 1.99 to 2.18.

Figure 6 shows the calculated ΔE values of TiO_2 :FCC films of Example 2 as a function of ratio of FCC to TiO_2 for FCCs with specific gravities ranging from 1.98 to 2.19.

Figure 7 shows tensile strength at break of TiO_2 :FCC films of Example 2 as a function of ratio of FCC to TiO_2 for FCCs with specific gravity ranging from 1.98 to 2.19.

Figure 8 shows Elmendorf tear strength of TiO_2 :FCC films of Example 2 as a function of ratio of FCC to TiO_2 for FCCs with specific gravity ranging from 1.98 to 2.19.

Detailed Description of the Invention

The polymer composition of the invention comprises a polymer resin. "Resin" is the general term used in the plastics art to denote a polymeric material (solid or liquid) prior to shaping into a plastic article.

The polymer resin used in the present invention is one which, on hardening (in the case of thermoplastic plastics) or curing (in the case of thermosetting plastics), forms a plastics material which has a refractive index of at least about 1.45. The refractive index is as measured by ASTM D542.

Preferred polymer resins are polyolefin resins, for example homopolymers of an olefin such as ethylene, propylene, butene or the like, or copolymers of an olefin monomer and another monomer. Typical examples of polyolefin homopolymers are polyethylene resins such as low-density polyethylene, middle-density polyethylene and high-density polyethylene, polypropylene resins, poly(4-methylpentene) resins and polybutene resins. Also suitable for use in the invention is linear low-density polyethylene (LLDPE) which although sometimes referred to as a homopolymer of ethylene is in fact an ethylene- α -olefin copolymer made by copolymerising ethylene with an α -olefin comonomer, normally butene, hexene or octene. Polyolefin copolymers which may be used in the present invention include polymers of two or more olefin monomers such as ethylene-polypropylene copolymer and copolymers of

ethylene or propylene with lower olefins such as butene-1, pentene-1, hexane or octene, as well as copolymers of an olefin monomer and another monomer, such as ethylene-vinyl acetate copolymer, ethylene-acrylic acid copolymer, ethylene-methacrylic acid copolymer. Mixtures of two or more different polyolefin copolymers are also contemplated, particularly mixes of LDPE and LLDPE.

Above all, polyethylene resins and blends thereof are preferable, and linear low-density polyethylene (ethylene- α -olefin copolymer) and low-density polyethylene are most preferable. Typical densities for these materials are as follows: 0.904 to 0.912 for ULDPE, 0.913 to 0.933 for LDPE, 0.915 to 0.942 for LLDPE and 0.949 to 0.964 for HDPE. Typical melt flow ratios are as follows: 0.25 up to 150, normally up to 20, typically up to 8 for LDPE; 0.5 up to 50, normally up to 20, and typically up to 10 for LLDPE; and 0.05 up to 30, normally up to 20 and typically up to 8 for HDPE.

The polyolefin resins used in the invention may be obtained by polymerization in a known way, e.g. by the use of a Ziegler catalyst, or obtained by the use of a single site catalyst such as a metallocene catalyst.

Examples of other plastics materials which may be used in accordance with the present invention are as follows, together with the refractive index:

	Epoxy resins	1.47
	Ethyl Cellulose	1.47
30	Acetal Homopolymer	1.48
	Acrylics	1.49
	Cellulose Nitrate	1.49 - 1.51
	Polyallomer	1.492
	Ionomers	1.51
35	Nylons (PA) Type II	1.52
	Acrylics Multipolymer	1.52

	Styrene Butadiene Thermoplastic	1.52 - 1.55
	PVC (Rigid)	1.52 - 1.55
	Nylons (Polyamide) Type 6/6	1.53
	Urea Formaldehyde	1.54 - 1.58
5	Styrene Acrylonitrile Copolymer	1.56 - 1.57
	Polystyrene	1.57 - 1.60
	Polycarbonate (Unfilled)	1.586
	Polysulfone	1.633

Preferred amongst these other polymer materials
 10 are PVC and epoxy resins.

As previously noted, the polymer composition of the invention includes as a co-opacifier with titanium dioxide, a flash calcined kaolin clay.

Calcined kaolin clay is normally prepared by heat-
 15 treating (calcining) a hydrous kaolin clay material. This serves to remove hydroxyl groups from the molecular structure (dehydroxylation). The calcination process typically causes significant modification of the crystal structure of the kaolin, leading to
 20 modification of the characteristics of the material. In particular, when a hydrous kaolin is calcined to about 500-600°C, an endothermic reaction occurs. Essentially all of the water associated with the uncalcined kaolin crystals is eliminated and an
 25 essentially amorphous (as measured by x-ray diffraction) material called metakaolin results. If the kaolin is heated to higher temperatures, further significant changes occur. The metakaolin undergoes an exothermic reaction (which typically occurs at about
 30 900-980°C). Such a material is then referred to as a "fully calcined kaolin".

The calcined kaolin used in the present invention is prepared by a flash calcination process, conducted on particles of hydrous kaolin. In the flash
 35 calcination process, the hydrous kaolin clay is heated at an extremely fast rate, almost instantaneously, e.g.

by exposure to a temperature greater than about 500°C for a time not more than 5 seconds, and typically less than 1 second. The temperature is suitably in the range of from 550°C to 1200°C.

5 Flash calcination of the hydrous kaolin particles (e.g. for less than about 1 second, for less than 0.5 second or for less than 0.1 second) gives rise to relatively rapid blistering of the particles caused by relatively rapid dehydroxylation of the kaolin. Water
10 vapour is generated during calcination, which may expand extremely rapidly, in fact generally faster than the water vapour can diffuse through the crystal structure of the particles. The pressures generated are sufficient to produce sealed voids as the
15 interlayer hydroxyl groups are driven off, and it is the swollen interlayer spaces, voids, or blisters between the kaolin platelets which typify flash calcined kaolins and give them characteristic properties.

20 The flash calcination process may be carried out by injecting the kaolin clay into a combustion chamber or furnace wherein a vortex is established to rapidly remove the calcined clay from the combustion chamber. A suitable furnace would be one in which a toroidal
25 fluid flow heating zone is established. For example, reference is made here to WO-A-99/24360, the contents of which are incorporated by reference in their entirety.

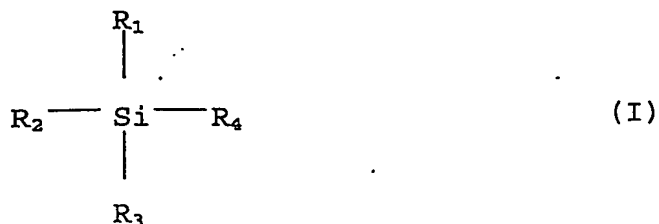
 Following calcination, the flash calcined clay may
30 be comminuted to the desired fineness and particle size distribution. Comminution may be achieved by use of conventional processing techniques such as sand grinding (e.g. wet sand grinding in suspension), milling (e.g. dry ball milling or fluid energy
35 milling), centrifigation, particle size classification, filtration, drying and the like. Wet sand grinding is

preferred, in which case the desired particle size reduction is typically achieved after a work input of about 110 kilowatt-hours per tonne, and the kaolin is then preferably filtered, dried at 80°C and milled to provide the final product.

The flash calcined kaolin used in the present invention typically has a specific gravity lower than hydrous kaolin, for example, equal to or less than 2.4, and desirably equal to or less than 2.2.

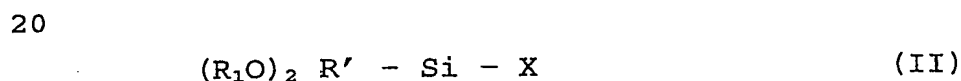
The flash calcined kaolin clay used in the invention is in particulate form and may suitably, but not essentially, have a particle size distribution such that at least about 40 weight % is below 2µm, and preferably up to about 75 weight % is below 2µm. More preferably, the flash calcined clay has a particle size distribution such that between about 50 and 65 wt.% are smaller than 2µm. The preferred d_{50} of the flash calcined clay is in the range of from about 1.4 to 2µm. For example, one presently preferred flash calcined clay for use in the invention may have about 55 wt.% of particles smaller than 2µm and a d_{50} of about 1.7 micron. In addition, the flash calcined clay for use in the invention may have a surface area in the range of from 5 to 25 m² per gram. (as measured by the BET liquid nitrogen absorption method ISO 5794/1), preferably about 10 to 20 m² per gram, and typically of the order of 12-14 m² per gram.

The particles of the flash calcined kaolin clay used in accordance with the present invention may be coated with an adherent coupling agent, which is preferably an organosilane coupling agents. Examples of suitable organosilane coupling agents include compounds of formula I:



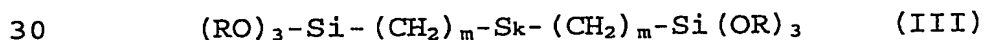
5 wherein R_1 is an aminoalkyl or mercaptoalkyl group, R_2 is a hydroxy, hydroxyalkyl or alkoxy group, and each of R_3 and R_4 , which may be the same or different, is a hydrogen atom or a hydroxy, alkyl, hydroxyalkyl or
 10 alkoxy group. Each of R_2 , R_3 and R_4 may, for example, be a hydroxy, hydroxyalkyl or alkoxy group, and each of R_1 , R_2 , R_3 and R_4 may, for example, contain not more than 4 carbon atoms. In one example, R_1 may be a γ -mercaptopropyl group and each of R_2 , R_3 and R_4 may be a
 15 methoxy group.

An alternative representation of examples of suitable organosilane coupling agents, which to some extent overlaps with formula I, is given by the following formula II:



wherein R' represents a C_{1-4} alkyl (e.g. methyl or ethyl) group, R_1 represents a methyl or ethyl group and
 25 X represents a mercaptopropyl group, a vinyl group or a thiocyanatopropyl group.

Still further examples of suitable organosilane coupling agents include compounds of formula III:



wherein R represents a C_{1-4} alkyl (e.g. methyl or ethyl) group and m and k are each independently selected from the integers 1, 2, 3, 4, 5 and 6 (e.g. $m = 3$ and $k =$
 35 4).

Still further examples of suitable organosilane coupling agents include compounds of formula IV:



(IV)

5

wherein X represents a C₁₋₄ alkoxy (e.g. methoxy or ethoxy) group or a chlorine atom, and R represents a glycidoxy, methacryl, amino, mercapto, epoxy or imide group.

10

Examples of preferred silanes for use in the invention are γ -aminopropyltriethoxy and vinyl-tris(2-methoxyethoxy)silane.

15

Preferably, the organosilane will be present in an amount up to about 2% by weight of the calcined clay n particles, more preferably from about 1% to about 1.5% by weight.

20

In addition to the flash calcined kaolin clay, the polymer composition of the invention, and products formed from it, also comprise titanium dioxide in a particulate form as an opacifier and white pigment. Particulate titanium dioxide for use as an opacifier in a polymer composition and products formed therefrom is widely available. Typically, however, the titanium dioxide used in this invention has a median aggregate size in the range of from about 0.2 to 0.35 μ m (as measured by x-ray disc centrifuge). Suitable titanium dioxide products which may be used in the invention are the Ti-Pure® range of materials from Du Pont.

25

30

The weight ratio of the flash calcined clay to the titanium dioxide in the composition should be in the range of up to about 10:1. More typically, the weight ratio of flash calcined clay to TiO₂ will be no greater than about 1:1. The preferred weight ratio of the flash calcined clay to the titanium dioxide in the composition is from about 1:100 to about 1:1, more

35

preferably from about 1:25 to about 1:1. The presently most preferred range is from about 1:3 to about 1:1.

The polymer composition of the present invention, and plastic products formed therefrom may additionally
5 comprise other particulate opacifying pigments, such as zirconium dioxide, zinc sulfide, antimony oxide, zinc oxide, lithopone (zinc sulfide + barium sulfate), barium sulfate, dolomite, magnesium silicate, calcium sulfate, calcium carbonate, alumina and quartz.

10 The polymer composition of the invention will normally be formed as a masterbatch (or concentrate) which is then let down, prior to use in a suitable product-forming step. Masterbatch compositions in accordance with the present invention may comprise up
15 to 90 wt.% of flash calcined clay and TiO_2 combined, based on the weight of the masterbatch (g flash calcined clay and TiO_2 per 100g of masterbatch), typically from 40 to 80 wt.% of the flash calcined clay and TiO_2 based on the weight of masterbatch.

20 Polymer compositions in accordance with the present invention which are to be used directly in a product-forming step may be prepared (let down) from a masterbatch, as described above, or formed directly to the appropriate composition. Such polymer compositions
25 should comprise a sufficient amount of flash calcined kaolin clay and TiO_2 to opacify the resultant composition, and the products formed therefrom. Although dependent on the polymer and the final application of the product, typically, the polymer
30 composition of the invention which is to be shaped into a plastics article may comprise up to about 30% by weight of combined flash calcined clay and TiO_2 opacifiers, preferably up to about 10% by weight, and will typically contain at least about 1% by weight of
35 the combined flash calcined clay and TiO_2 opacifier. For polyethylene film applications, the amount of flash

calcined clay and TiO_2 opacifier is preferably in the range of from 1 to 10% by weight.

The polymer compositions of the present invention may comprise further additives, well known in the plastics art. Amongst the further additives which may be included are bonding or tackifying agents, plasticisers, lubricants, anti-oxidants, Ultraviolet absorbers, dyes, colourants, processing stabilisers and processing aids.

The present invention also contemplates polymer compositions, and products formed therefrom, which further comprise a predominant particulate filler material. For example, moisture permeable, or "breathable" polyolefin film, particularly breathable polyethylene and polypropylene films, comprises a substantial proportion of a inorganic material, normally a calcium carbonate filler, which may be present in an amount of the order of up to about 70 wt.% in the composition from which the film product is formed and in the film itself. It is known that such compositions may also comprise an opacifying amount of a TiO_2 . In accordance with the present invention, such compositions may also include a flash calcined clay as a co-opacifier in combination with the TiO_2 .

The polymer resin, flash calcined kaolin clay and titanium dioxide and, if necessary, other optional additives, may be formed into a suitable masterbatch by the use of a suitable compounder/mixer in a manner known per se, and may be pelletized, e.g. by the use of a single screw extruder or a twin-screw extruder which forms strands which may be cut or broken into pellets. The compounder may have a single inlet for introducing the flash calcined kaolin clay, the titanium dioxide and the polymer together. Alternatively, separate inlets may be provided for the opacifier components and

the polymer resin. Suitable compounders are available commercially, for example from Werner & Pfleiderer.

As an alternative to forming a single masterbatch, the titanium dioxide and the flash calcined clay may be formed into separate masterbatches, which are then combined and made down in suitable proportions to form the final polymer composition from which the plastics article is to be made.

The polymer composition of the present invention, having an appropriate concentration of opacifier for the intended end use, may be shaped in a suitable molding process to form a plastics product. Examples of plastics products which may be formed from the polymer composition of the invention include polyolefin films, and in particular polyethylene (such as LDPE and LLDPE) films, as well as non-film products such as opaque plastic containers, bottles, etc. The present invention is particularly suited to making plastic film, which may then be used in wide variety of end uses, such as bags, packaging material, wrapping paper, pouches, agricultural film, etc. Such films typically have a thickness which may be in the range of up to 500µm, more often up to 300µm, and normally in the range of from 20 to 80µm.

Plastics products may be formed in a wide variety of shaping procedures, such as, for example, extrusion, injection molding, compression molding, blow molding and casting. The preferred plastic films of the present invention may, for example, be made by casting the film using a flat die or by blow molding the film using a tubular die. The polymer composition of the invention may also be co-extruded into multilayer films with other polymers both in cast and blown film processes. Suitable other polymers for co-extrusion in this respect may be nylon, polyethylene (all types), polyvinyl acetate and polyvinyl alcohol, PVC and PVdC,

PET, OPP, as well as suitable adhesive layers. In extrusion methods for making plastics film, the film may be extruded onto a set of rollers that smooth and stretch the film. This stretching or orientation stage may, for example, be done in MD only, TD only or both using a variety of flat film orientation processes such as stretching using flat rollers, inter-digitated rollers, tenter frames or tenter chains. The film may be, alternatively oriented using tubular orientation processes (which is normally used for blown film).

In addition the plastic films may be modified to improve surface properties for ease of printing, film lamination, and/or film adhesion using a selection of processes such as: corona treatment, flame treatment, priming or sub-coating, use of adhesives, solvents or coatings.

The invention will now be illustrated with reference to the following non-limiting examples.

Example 1

Polyethylene compositions for film production were prepared from three masterbatches, a TiO_2 masterbatch nominally comprising 60 wt.% TiO_2 , a flash calcined clay (hereafter FCC) LDPE/LDPE (50:50) masterbatch nominally comprising 15 wt.% FCC and a silane treated FCC (hereafter TFCC) LDPE/LDPE (50:50) masterbatch comprising 15 wt.% TFCC. The TiO_2 masterbatch was obtained as a commercially available product. The FCC masterbatch was prepared using a twin screw extruder at an FCC loading of 15 wt.%, also including an antioxidant in an amount of 0.1g per 100g of resin. The FCC had a particle size distribution as follows: 4% larger than $10\mu\text{m}$; 5% larger than $8\mu\text{m}$, 12% larger than $5\mu\text{m}$, 55% smaller than $2\mu\text{m}$, 30% smaller than $1\mu\text{m}$, 15% smaller than $0.75\mu\text{m}$ and less than 5% smaller than $0.5\mu\text{m}$, and a typical d_{50} value of $1.6\mu\text{m}$. The TFCC

masterbatch was prepared in the same way as the FCC masterbatch, using a similar FCC to that used for the FCC masterbatch, coated with 2% by weight γ -propyltriethoxysilane.

5 Final formulations were obtained by dilution of TiO_2 , FCC and TFCC masterbatches (60%, 15% and 15% by weight respectively) using a twin screw extruder (Baker Perkins MP2000). The polymer system used to dilute the masterbatches was the same 50:50 blend of LDPE and
10 LLDPE used to prepare the FCC and TFCC masterbatches. Antioxidant Irganox 1076 (Ciba) was added at 0.10 g per 100 grams of polymer. All compounding was done at a screw speed of 350 rpm; feed rates to the compounder were adjusted to 8 to 12 kg.h^{-1} to maintain constant
15 torque and stable processing.. Selected temperatures of 190 (die), 180, 170, 165, 160 and 155°C were used which allowed a melt temperature at the die of 195 to 197 for FCC compounds and 195 to 201 for TFCC compounds.

20 Films with a nominal thickness of 50 μm were blown using a Betol SK 32 Line with a screw speed of 56 rpm and a layflat width of 225mm, which corresponds to a BUR of 2.8.

 A variety of films were prepared as detailed in
25 Table 1 below comprising mixes of from 2 to 3.6 wt.% TiO_2 and from 0.8 to 2 wt.% FCC (Films 1b to 1g) or TFCC (Films 2b to 2g) together with films comprising 4 wt.% TiO_2 or 4 wt.% FCC (or TFCC). These were nominal loadings; the actual filler loadings were also measured
30 by loss on Ignition at 650 °C for 1 hr. Measurement was repeated 5 times for each film formulation and results averaged. All filler loadings are given in Table 1 in weight percentage. The measured filler levels are $\pm 0.4\%$.

Table 1

Film ID	TiO ₂	FCC	Total _{Target}	Filler _{measured}
1a	4.0	0.0	4.0	3.99
1b	3.6	0.4	4.0	3.96
1c	3.6	0.8	4.4	4.52
1d	3.6	1.2	4.8	4.88
1e	3.6	1.6	5.2	5.28
1f	3.2	0.8	4.0	4.26
1g	2.0	2.0	4.0	4.30
1h	0.0	4.0	4.0	4.33
2b	3.6	0.4	4.0	4.42
2c	3.6	0.8	4.4	4.82
2d	3.6	1.2	4.8	5.26
2e	3.6	1.6	5.2	5.37
2f	3.2	0.8	4.0	3.89
2g	2.0	2.0	4.0	5.87
2h	0.0	4.0	4.0	4.41

Film specimens were conditioned at 23°C and 50% RH for 48 hours prior to optical and mechanical measurements.

5 Opacity

Measurement of the opacity of films made with the untreated flash-calcined clay provided the values shown in Table 2 below. Opacity was measured by the contrast ratio method using a Minolta CM-361 Spectrophotometer.

Measurements were made using paraffin oil, with a refractive index close to that of LDPE and LLDPE, to eliminate the effect of surface defects on the film (scratches, due to flow instabilities, filler protruding from film) on optical properties. Due to the sensitivity of opacity to film thickness variation the measured opacity values were normalized to a film thickness of 50µm.

Table 2

Film ID	wt % TiO ₂	wt % FCC	L / μ m	Opacity	Op ^{corrected}
1a	4	0	52.1	68.0	67.3
1b	3.6	0.4	50.0	65.8	65.8
1c	3.6	0.8	50.1	66.7	66.7
1d	3.6	1.2	49.4	66.6	66.8
1e	3.6	1.6	47.9	66.3	67.0
1f	3.2	0.8	51.4	66.3	65.8
1g	2	2	52.1	59.1	--
1h	0	4	48.9	19.3	--
2b	3.6	0.4	49.2	66.3	66.6
2c	3.6	0.8	48.4	66.3	66.8
2d	3.6	1.2	49.1	65.9	66.2
2e	3.6	1.6	50.0	66.7	66.7
2f	3.2	0.8	49.0	62.7	--
2g	2	2	48.4	65.6	--
2h	0	4	51.4	31.0	--

Results are also presented in Figure 1 which shows opacity as a function of the level of FCC for film with 3.6% TiO₂. The broken line represents the value at 0% FCC, 4% TiO₂. These values indicate that, upon replacement of 10% TiO₂, in order to recover the opacity value of the original film, the amount of added FCC must be 4 times that of the replaced TiO₂.

Transmittance/Colour

The transmittance of the films comprising the untreated FCC was also measured to check the opacity data obtained, as were the haze and clarity. The results obtained are set forth in Table 3 below. Transmittance (T), haze (H), and clarity (C) were measured with a BYK-Gardner Haze Gard-plus meter following a method that conforms to ASTM D-1003 and D-1044. T_L^C is the standardized transmittance for a standard thickness of 50 μ m and the target weight of

filler. Filler percentage are in weight % and L is the thickness of the film in microns.

Table 3

ID	% TiO ₂	% FCC	L / μm	T / %	T _L ^C	H	C
1a	4.0	0.0	51.3	46.9	47.8	>99	55.3
1b	3.6	0.4	49.8	48.9	48.8	>99	62.9
1c	3.6	0.8	49.5	48.5	48.1	>99	56.3
1d	3.6	1.2	49.8	46.5	46.4	>99	49.8
1e	3.6	1.6	49.6	46.9	46.6	>99	42.0
1f	3.2	0.8	50.9	47.1	47.7	>99	51.4
1g	2.0	2.0	50.8	55.2	55.7	>99	62.2
1h	0.0	4.0	51.9	87.7	88.1	59.7	57.9
2b	3.6	0.4	49.7	47.7		>99	65.0
2c	3.6	0.8	49.7	46.0		>99	53.9
2d	3.6	1.2	50.9	47.0		>99	59.3
2e	3.6	1.6	50.7	45.6		>99	42.4
2f	3.2	0.8	50.4	51.8		>99	72.2
2g	2.0	2.0	50.3	48.5		>99	52.4
2h	0.0	4.0	51.4	79.8		78.1	59.5

Results are also presented in Figure 2 which shows transmittance of films containing 3.6 % by weight TiO₂ as a function of the level of FCC. The broken line represents the value at 0 % FCC, 4 % by weight TiO₂. All values are normalised to 50 μm film thickness. Error bars correspond to 2 standard deviations. Figure 2 shows upon replacement of 10 % TiO₂ the level of transmittance of the original film is recovered when the level of added FCC is approximately 3 to 4 times that of the substituted TiO₂. Within experimental error this is in agreement with the observations on film opacity.

Measurements were also made of the colour of untreated FCC-filled film. Colour was measured using Minolta CM-361 Spectrophotometer. Colour measurements of TiO₂ / FCC films are set forth in Table 4 below. ΔE

corresponds to Brightness and is calculated from values of L^* , a^* , and b^* ,

Table 4

ID	% TiO ₂	% FCC	L*	a*	b*	C*	h	ΔE
1a	4.0	0.0	96.9	-0.13	2.44	2.45	93.0	3.97
1b	3.6	0.4	96.5	-0.11	2.6	2.60	92.5	4.39
1c	3.6	0.8	96.3	-0.09	2.65	2.65	92.0	4.57
1d	3.6	1.2	95.8	-0.08	2.78	2.78	91.6	5.05
1e	3.6	1.6	95.6	-0.05	2.94	2.95	91.0	5.32
1f	3.2	0.8	96.2	-0.09	2.66	2.66	92.0	4.68
1g	2.0	2.0	95.0	-0.02	3.14	3.14	90.4	5.92
1h	0.0	4.0	87.6	0.19	5.34	5.35	87.9	13.5

- 5 Table 4 shows colour parameters for all films containing FCC. Reference to this table illustrates that the addition of FCC to substitute the TiO₂ increases the yellowness of the film, as indicated by the increase in b^* values with FCC concentration.
- 10 Changes in L^* , a^* , and b^* are summarised when we observe changes in the brightness values, ΔE . A significant change in brightness is observed with increasing levels of added FCC.

- 15 Colour measurements were also made of the treated FCC-filled film. The results obtained are set forth in Table 5 below.

Table 5

ID	% TiO ₂	% FCC	L*	a*	b*	C*	h	ΔE
2b	3.6	0.4	96.5	-0.14	2.47	2.48	93.3	4.31
2c	3.6	0.8	96.4	-0.13	2.67	2.67	92.9	4.46
2d	3.6	1.2	96.1	-0.14	2.65	2.66	93.0	4.72
2e	3.6	1.6	96.2	-0.13	2.88	2.88	92.5	4.78
2f	3.2	0.8	96.6	-0.14	2.68	2.69	93.1	4.36
2g	2.0	2.0	96.0	-0.13	2.92	2.93	92.6	4.93
2h	0.0	4.0	92.6	-0.19	4.52	4.53	92.4	8.66

A yellowing test for discolouration at 85°C in the presence of nitrogen oxides was also conducted on the untreated FCC films. The results of this test (not shown) indicate that after a 2-hour period exposure to NO_x gasses none of the samples showed discoloration.

Mechanical Properties

The mechanical properties of the films were also measured to determine whether these are affected by the level of substitution of TiO₂. Tensile strength was measured according to ASTM D 882-91. The results obtained are set forth in Tables 6 (tensile properties of films in machine direction) and 7 (tensile properties of films in transverse direction) below

Table 6

ID	TiO ₂	CC	L / μm	El / %	Error	S _b / MPa	Error	BF / Nm^{-1}	Error
1a	4.0	0.0	51.2	643	27	28.4	2.5	1456	125
1b	3.6	0.4	50.7	602	13	25.2	1.6	1300	128
1c	3.6	0.8	50.8	611	27	24.8	1.8	1259	106
1d	3.6	1.2	51.1	571	15	24.5	1.2	1254	99
1e	3.6	1.6	53.8	582	38	25.3	1.7	1357	68
1f	3.2	0.8	48.7	619	12	25.8	1.1	1260	94
1g	2.0	2.0	50.5	555	22	29.3	2.1	1478	91
1h	0.0	4.0	49.7	556	12	29.9	1.9	1486	105
2b	3.6	0.4	52.4	634	24	27.5	1.5	1442	103
2c	3.6	0.8	56.2	636	38	25.8	1.9	1456	233
2d	3.6	1.2	54.5	636	11	26.0	1.5	1420	141
2e	3.6	1.6	59.0	654	27	26.5	2.2	1570	194
2f	3.2	0.8	55.6	614	10	26.0	1.4	1449	155
2g	2.0	2.0	57.3	647	22	25.1	1.6	1443	155
2h	0.0	4.0	57.5	582	27	25.1	1.7	1441	73

Table 7

ID	TiO ₂	CC	L / μ m	El / %	Error	S _b /MPa	Error	BF /Nm ⁻¹	Error
1a	4.0	0.0	51.1	609	37	22.7	2.4	1154	126
1b	3.6	0.4	53.3	597	18	20.6	1.6	1105	114
1c	3.6	0.8	50.9	584	40	20.8	2.2	1060	111
1d	3.6	1.2	52.1	586	27	20.1	1.3	1048	67
1e	3.6	1.6	52.5	608	31	22.2	1.7	1162	83
1f	3.2	0.8	50.8	623	26	23.8	1.1	1209	81
1g	2.0	2.0	51.1	571	23	25.9	1.7	1324	139
1h	0.0	4.0	48.9	554	34	26.1	2.7	1280	188
2b	3.6	0.4	54.0	595	22	22.6	1.7	1222	154
2c	3.6	0.8	55.3	607	33	22.0	0.6	1218	102
2d	3.6	1.2	54.3	599	27	22.5	1.3	1227	142
2e	3.6	1.6	54.8	594	42	22.2	2.4	1224	206
2f	3.2	0.8	55.6	615	11	26.1	1.5	1453	157
2g	2.0	2.0	52.9	587	38	19.7	2.6	1040	156
2h	0.0	4.0	57.1	563	43	18.6	2.1	1063	156

Reference to Figure 3 shows that the mechanical properties of the films are not affected by the level of substitution of TiO₂. This is the case for all tensile properties in both MD and TD. The values are very similar for films with compositions varying from 4 % TiO₂ to 4 % FCC. This fact reflects the dominant effect of the resin in the tensile properties of these films where it represents 98 to 99 % by volume.

In this example it is shown that FCC and silane-treated FCC may be used as a substitute for TiO₂ in plastic film. At 10 % substitution it is possible to recover the opacity and transmittance of the original 4 % TiO₂ film by adding extra FCC to the film (3 to 4 times that of the replaced TiO₂). Haze is not affected and remains very high. A slight deterioration of colour and clarity is observed. However, addition of FCC does not affect the resistance of the film to

discoloration. Mechanical properties of the film are not affected by FCC addition.

Example 2

Four different flash calcined clays (FCC1, FCC2, FCC3 and FCC4 having specific gravities of 2.08, 2.19, 2.03 and 1.98 respectively) were compounded into LLDPE having a MFI of 20 using a twin-screw extruder (Baker Perkins MP200) to produce 40wt.% masterbatches. The processing conditions are set forth in Table 8 below.

Table 8

Masterbatch ID	Temperature / °C						Torque / %
	Die	5	4	3	2	1	
FCC1 (SG = 2.08)	200	188	177	162	165	150	30
FCC2 (SG = 2.19)	200	188	177	162	165	150	30
FCC3 (SG = 2.03)	205	190	178	185	170	165	25
FCC4 (SG = 1.98)%	201	177	170	164	165	160	25

All Masterbatches were prepared in Exxon Escorene LLDPE resin LL6101 XR (MFI = 20, density 0.924), with antioxidant Irganox1076 added at 0.15 g per 100 g resin. Processing with selected temperatures of 190 (die), 180, 170, 165, 155, and 145 °C. Extruder operating at 350rpm except for FCC4, for which a screw speed of 300rpm was employed. Throughput was in the range 6 to 8kg/hr.

These masterbatches, together with a TiO₂ masterbatch, were let down with Exxon Escorene LLN1001XV (MFI of 1) to achieve a total filler concentration (FCC and TiO₂) of 4wt% using a Baker Perkins twin screw extruder operating at 350rpm and a throughput in the range 10 to 14 kg/hr and selected temperatures of 190 (die), 180, 170, 165, 155, and 145°C. For each FCC, compounds were prepared having the following FCC to TiO₂ ratios: 40:30, 30:40, 43:27 and 45:25. Filler loading was measured by loss on ignition at 650 °C, except for TiO₂/CaCO₃ films for

which 450 °C was used. Irganox 1016 was added as a stabiliser at a level of 0.15g antioxidant per 100g of resin. Film processing was carried out using a Betol SK 32 operating at a screw speed of 56 rpm (10 A load) and a haul-off rate of 7 m / min. Film was made at a nominal thickness of 50 micron, and a lay-flat of 225 mm.

Film specimens were conditioned at 23°C and 50% RH for 48 hours prior to optical and mechanical measurements as in Example 1.

Opacity

The opacity of the TiO₂:FCC films as a function of FCC/TiO₂ ratio for FCCs with SGs ranging from 1.99 to 2.19 was measured and the results are shown in Figure 4. All films contain 4 wt.% total filler content. The opacity values are not corrected for filler loading or film thickness and are, therefore, subjected to relatively large errors (\pm 1-2 opacity units).

Transmittance/Colour

Transmittance was also measured as in Example 1 and the results, obtained for the same films as in Figure 4 are illustrated in Figure 5. Transmittance values are corrected for thickness and filler loading. These values were normalised to a film thickness of 50 μ m and a total filler loading of 4 wt%. Figure 5 shows that the reported values are subjected to large errors (this is also evidenced during normalisation of the values for thickness and concentration).

Colour measurements were also made of the films and the results are summarised in Figure 6, which shows the calculated ΔE (which takes account of L, a and b values) of TiO₂:FCC films as a function of the ratio of FCC to TiO₂ for FCCs with specific gravity ranging from 1.98 to 2.19. The composition of films was as for Figure 4. These results show that increasing the level

of TiO_2 substitution decreases brightness and increases b values (yellowness).

Mechanical Properties

In order to determine the mechanical properties of the films, the tensile strength and Elmendorf tear strength were measured according to ASTM D 882-91 and ASTM D 1922-94a respectively. QUV (UVA) testing was conducted according to ASTM D 4329-92.

Figure 7 shows tensile strength at break of TiO_2 :FCC films as a function of ratio of FCC to TiO_2 for FCCs with specific gravity ranging from 1.98 to 2.19. The composition of films was as for Figure 4. In Figure 7, the left hand bar of each group corresponds to FCC1, the left middle bar corresponds to FCC2, the right middle bar corresponds to FCC3 and the right hand bar corresponds to FCC4. Error bars correspond to 2 standard deviations. Within experimental error, tensile strength is not affected by partial substitution of TiO_2 by FCC. In addition, reference to Figure 7 also shows that the SG of the clay has no effect on tensile strength.

Figure 8 shows Elmendorf tear strength of TiO_2 :FCC films as a function of ratio of FCC to TiO_2 for FCCs with specific gravity ranging from 1.98 to 2.19. Again, the composition of films was as for Figure 4. In Figure 8, the left hand bar of each group corresponds to FCC1, the left middle bar corresponds to FCC2, the right middle bar corresponds to FCC3 and the right hand bar corresponds to FCC4. Error bars correspond to 2 standard deviations. As with tensile strength partial substitution of TiO_2 by FCC has no significant effect on tear strength.

All references cited herein are expressly incorporated by reference for all purposes.

The foregoing broadly describes the present invention, without limitation. Variations and

modifications as will be readily apparent to one of ordinary skill in this art are to be considered as included within the scope of this application and any subsequent patent(s).

5

CLAIMS

1. A polymer composition comprising a polymer resin, a flash calcined kaolin clay filler and a titanium dioxide filler, wherein the weight ratio of the flash calcined clay to the titanium dioxide, in the composition is in the range of up to 10:1 and wherein the polymer resin is one which hardens or cures to a plastic material which has a refractive index of at least about 1.45.
2. A polymer composition according to claim 1, wherein the polymer resin is a polyolefin resin.
3. A polymer composition according to claim 2, wherein the polyolefin resin is a homopolymer of an ethene, propene or butene or a copolymer of ethane, propene, butene and another monomer.
4. A polymer composition according to claim 3, wherein the polyolefin resin is a polyethylene resin.
5. A polymer composition according to claim 4, wherein the polyethylene resin is selected from low density polyethylene, linear low-density polyethylene, middle-density polyethylene and high density polyethylene.
6. A polymer composition according to claim 5, wherein the polyethylene resin is selected from low-density polyethylene and linear low density polyethylene.
7. A polymer composition according to claim 1, wherein the polymer resin is a PVC resin.
8. A polymer composition according to any preceding claim, wherein the flash calcined clay has a specific gravity no greater than 2.4.
9. A polymer composition according to claim 8, wherein the flash calcined clay has a specific gravity no greater than 2.2.
10. A polymer composition according to any preceding claim, wherein the flash calcined clay has a

particle size distribution such that at least 50 weight % of the particles are smaller than 2 μ m.

11. A polymer composition according to claim 10, wherein the flash calcined clay has a particle size
5 distribution such that between about 40 and 80 weight % of the particles are smaller than 2 μ m.

12. A polymer composition according to any preceding claim, wherein the flash calcined clay has a d_{50} in the range of from about 1.4 to 2.0 μ m.

10 13. A polymer composition according to claim 4, 5 or 6, wherein the flash calcined clay has a specific gravity of less than about 2.4, a particle size distribution such that between about 50 and 65 weight % of the particles are smaller than 2 μ m and a d_{50} in the
15 range of from about 1.4 to 2.0 μ m.

14. A polymer composition according to any preceding claim, wherein the flash calcined clay is obtained by exposing a particulate hydrous kaolin clay to a temperature of greater than about 500°C for a time
20 not more than 5 seconds.

15. A polymer composition according to any preceding claim, wherein the flash calcined clay is coated with an adherent coupling agent.

16. A polymer composition according to claim 15,
25 wherein the adherent coupling agent is an organosilane coupling agent.

17. A polymer composition according to any preceding claim, wherein the TiO₂ has a median aggregate size in the range of from about 0.2 to 0.35
30 μ m.

18. A polymer composition according to any preceding claim, wherein the weight ratio of the flash calcined clay to TiO₂ is in the range of from about 1:100 to about 1:1.

19. A polymer composition according to claim 18, wherein the weight ratio of the flash calcined clay to TiO_2 is in the range of from about 1:25 to about 1:1.

20. A polymer composition according to claim 18, wherein the weight ratio of the flash calcined clay to TiO_2 is in the range of from about 1:3 to about 1:1.

21. A polymer composition according to any preceding claim, comprising up to about 80% of the combined weight of the flash calcined clay and titanium dioxide, based on the total weight of the composition.

22. A polymer composition according to claim 21, comprising from about 40 to about 80% of the combined weight of the flash calcined clay and titanium dioxide, based on the total weight of the composition.

23. A polymer composition according to claim 21, comprising up to about 30% of the combined weight flash calcined clay and titanium dioxide, based on the total weight of the composition.

24. A polymer composition according to claim 23, comprising from about 1 to about 10% of the combined weight of the flash calcined clay and titanium dioxide, based on the total weight of the composition.

25. A polymer composition according to any preceding claim, comprising an inorganic filler component.

26. A polymer composition according to claim 25, wherein the inorganic filler is a calcium carbonate.

27. A polymer composition comprising a polyethylene resin, a flash calcined clay and a titanium dioxide, wherein the weight ratio of the flash calcined clay to the titanium dioxide is in the range for from 1:100 to 1:1.

28. A polymer composition according to claim 27, wherein the weight ratio of the flash calcined clay to TiO_2 is in the range of from about 1:25 to about 1:1.

29. A polymer composition according to claim 28, wherein the weight ratio of the flash calcined clay to TiO_2 is in the range of from about 1:3 to about 1:1.

30. A polymer composition according to claim 27,
5 28 or 29, comprising up to about 80% of the combined weight of the flash calcined clay and titanium dioxide, based on the total weight of the composition.

31. A polymer composition according to claim 30, comprising from about 40 to about 80% of the combined
10 weight of the flash calcined clay and titanium dioxide, based on the total weight of the composition.

32. A polymer composition according to claim 30, comprising up to about 30% of the combined weight flash calcined clay and titanium dioxide, based on the total
15 weight of the composition.

33. A polymer composition according to claim 30, comprising from about 1 to about 10% of the combined weight of the flash calcined clay and titanium dioxide, based on the total weight of the composition.

20 34. A plastic article formed from a polymer composition of any preceding claim.

35. A plastic article according to claim 34 which is a polyolefin film.

25 36. A plastic article according to claim 35 which is a polyethylene film.

37. A production process for preparing the polymer composition of claim 1, wherein the polymer resin, the flash calcined kaolin clay and the titanium dioxide are combined together to form a homogenous
30 composition.

38. A production process according to claim 37, wherein the flash calcined kaolin clay and the titanium dioxide are mixed with the polymer resin to form a homogenous composition.

35 39. A production process according to claim 38, wherein separate premixes of (a) the polymer resin and

flash calcined clay and (b) the polymer resin and the titanium dioxide are formed, which are then combined, optionally together with additional polymer resin.

40. A polymer composition comprising a polyolefin resin and an opacifying amount of a mixture of titanium dioxide and a flash calcined kaolin clay.

41. A polyolefin film comprising an opacifying amount of a mixture of a flash calcined clay and a TiO_2 .

10

ABSTRACTAN OPACIFIED POLYMER COMPOSITION

There is disclosed a polymer composition comprising a polymer resin and, as opacifier, a flash
5 calcined kaolin clay filler and a TiO_2 . The polymer composition may be formed into shaped articles, particularly polyolefin film.

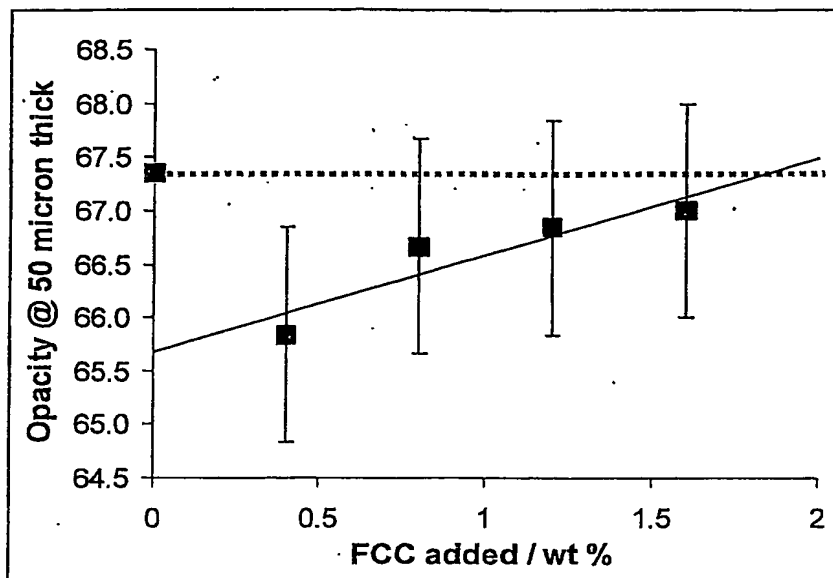


Figure 1

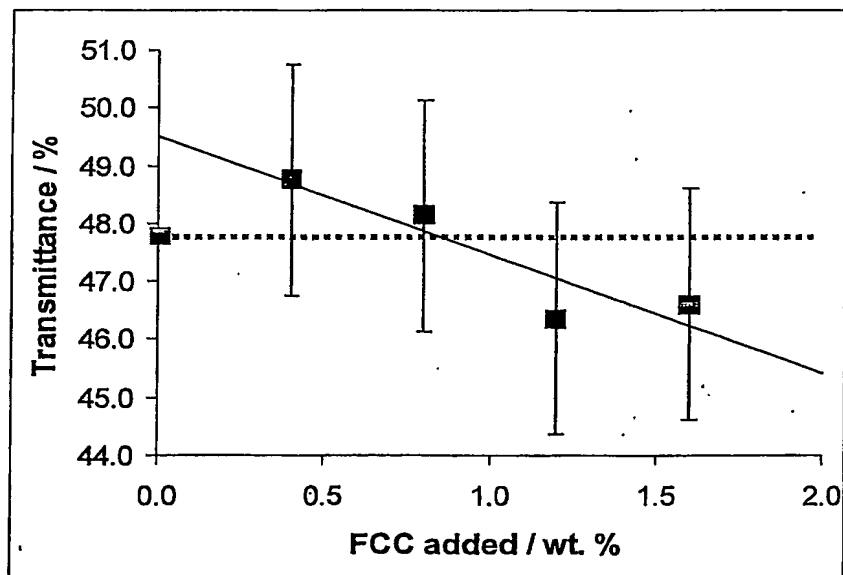


Figure 2

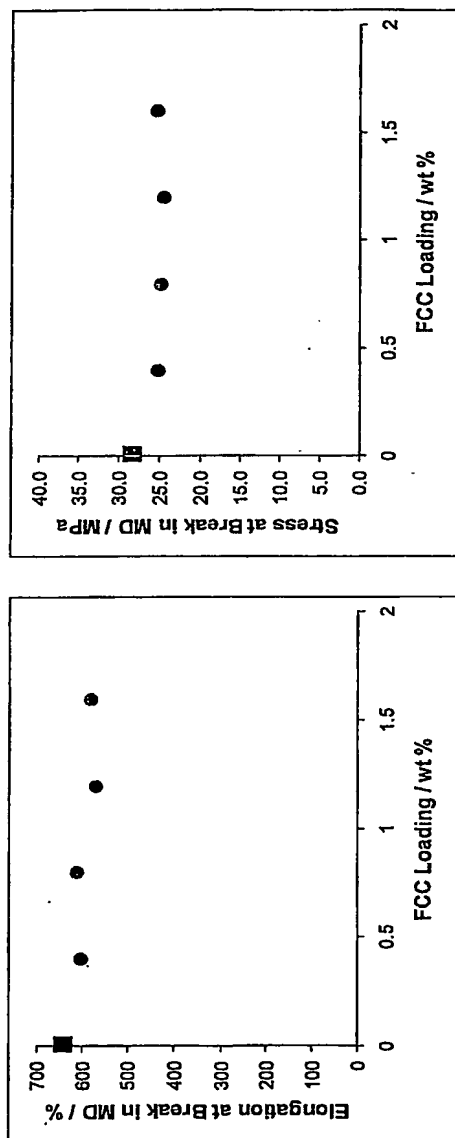


Figure 3

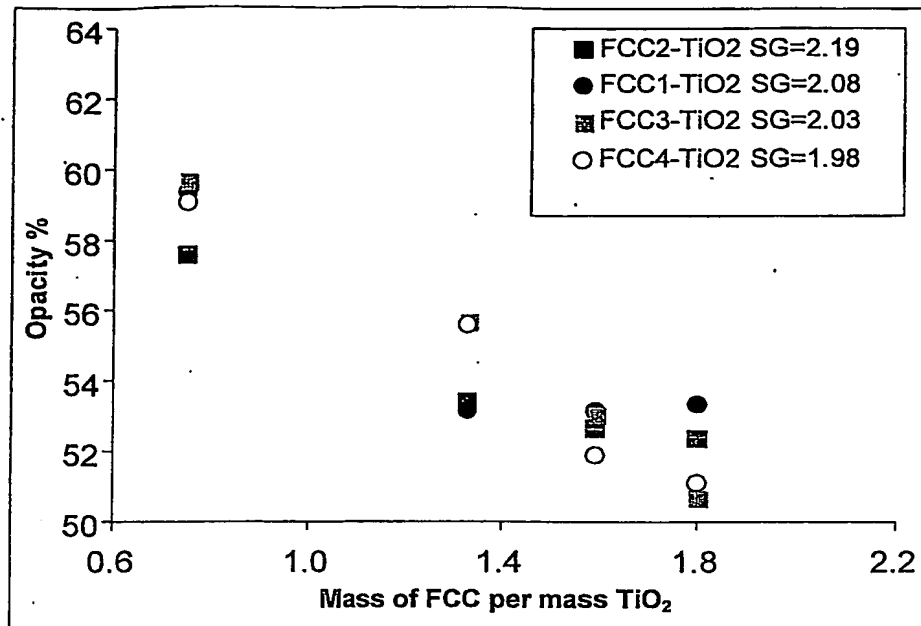


Figure 4

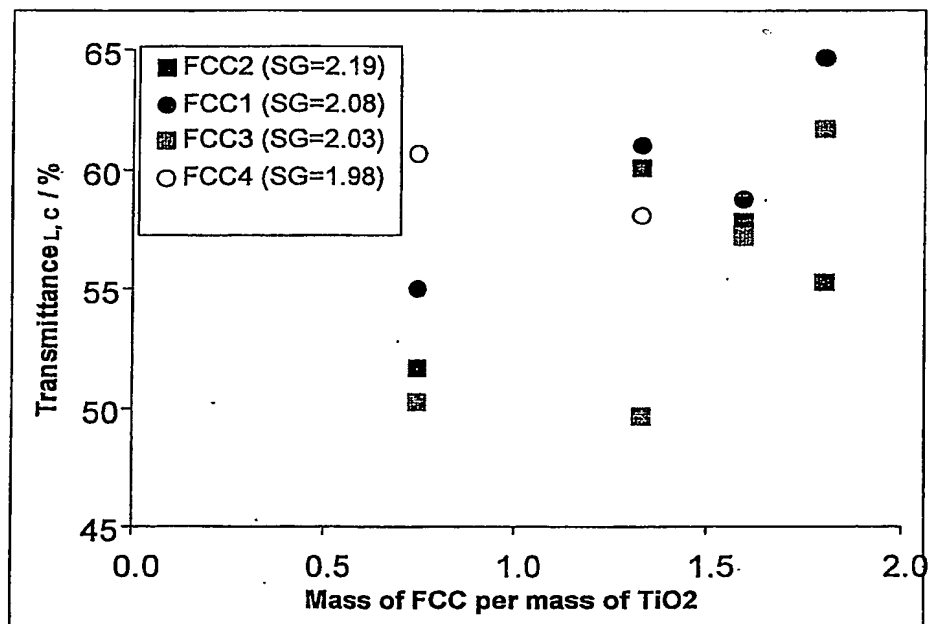


Figure 5

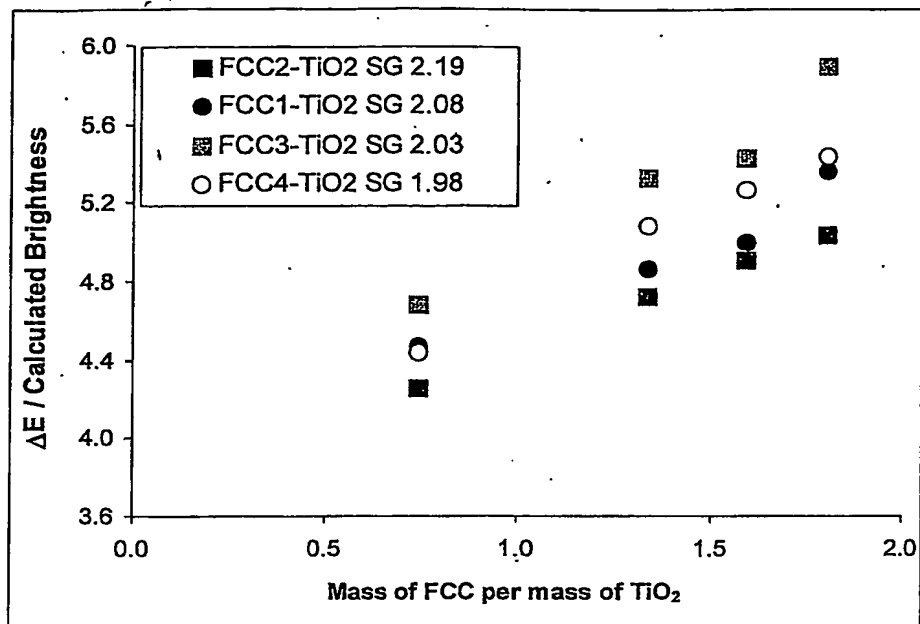


Figure 6

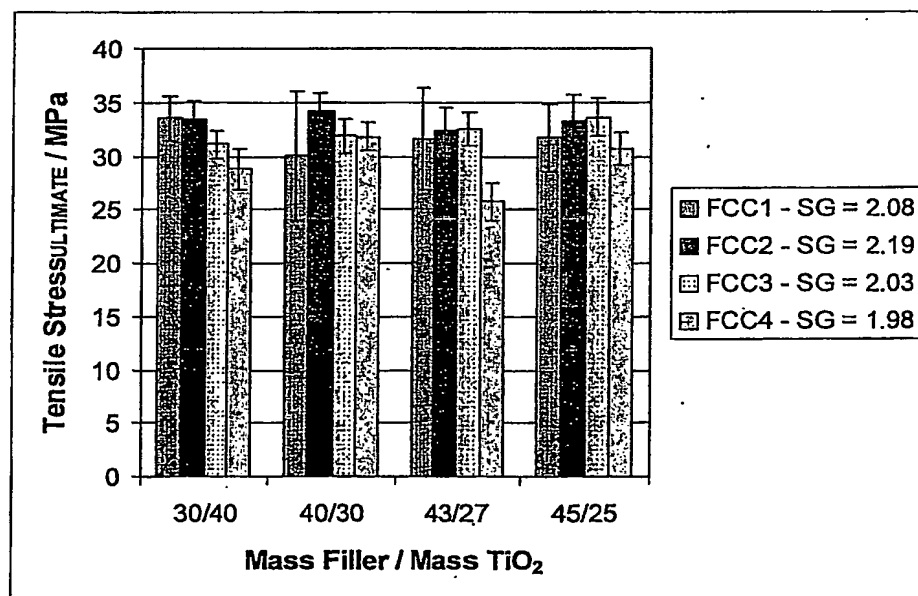


Figure 7

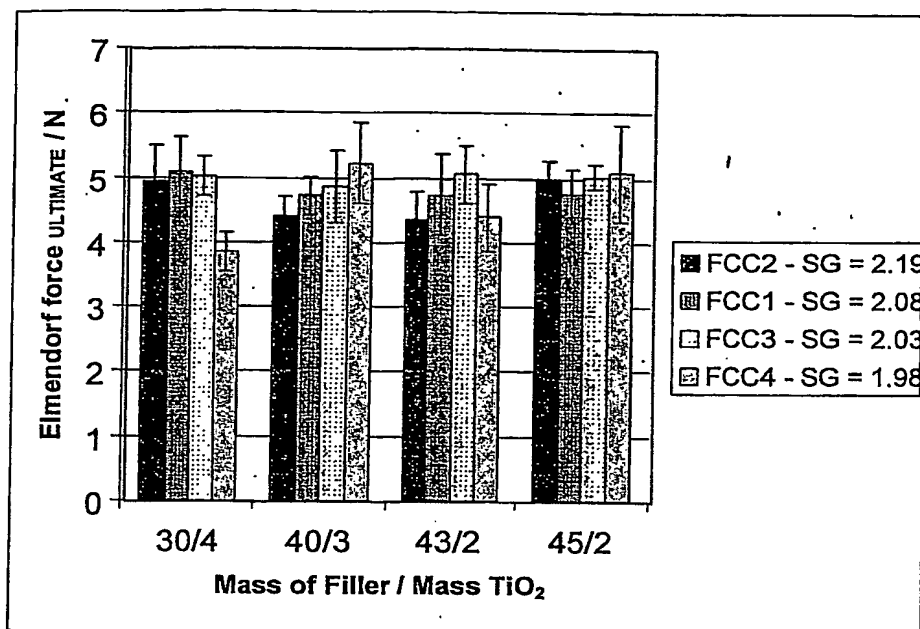


Figure 8

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